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The Influence of the Bleaching Medium on Caustic Extraction Efficiency (II): Oxidized Lignin Solubility

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THE INFLUENCE OF THE BLEACHING MEDIUM ON CAUSTIC EXTRACTION EFFICIENCY (II): OXIDIZED LIGNIN SOLUBILITY

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ABSTRACT

Caustic extractions performed with >50% ethanol solutions severely hindered lignin removal from chlorine dioxide (D_0) treated pulps. In this study, we show that the alkali solubility of an isolated D_0 lignin decreased as the concentration of ethanol in the medium was increased from 50 to 75%. In addition, the amount of dissolved lignin in the alkaline extraction effluents approached its solubility limit when the medium contained more than 50% ethanol. These results indicate that alkaline extractions of D_0-stage pulps with ethanol-rich media were limited by the lower solubility of *ionized* lignin fragments in these solutions as compared to water. An empirical solubility parameter analysis predicted that *non-ionized* D_0 lignins should be more soluble in ethanol than in water. Indeed, delignification with an acid extraction stage was improved when the water was replaced with ethanol.

INTRODUCTION

Environmental pressures on the pulp and paper industry have spurred considerable research into developing new pulp manufacturing processes that have minimum impact on the environment. Much of this research has focused on alternative

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pulping and bleaching methods. Of particular interest to us is the application of organic solvents to pulping and bleaching processes.[1-5] The addition of organic solvents to aqueous solutions may provide more selective processes for removing residual lignin. Recent studies of ozone bleaching have indicated that bleaching selectivity can be greatly improved by employing an organic solvent-water mixture instead of water as the impregnating medium.[3,4] However, the use of non-aqueous media for other oxidative and/or extraction stages has not been studied.

We have examined bleaching of softwood kraft brownstock pulps in the presence of ethanol with chlorine dioxide (D_0) and caustic extraction (E) stages.[6,7] Experiments showed (1) that delignification was decreased by ~60% when the ethanol concentration in the alkaline extraction stage was increased from 50 to 85% (v/v) and (2) that the decrease was not caused by the reduced mobility of lignin fragments within the fiber wall as a result of fiber de-swelling.[6,7] In this paper, we examine whether the observed reduction in E-stage delignification is due to a lower solubility of D_0 lignin in alkaline ethanol-water solutions as compared to water. In addition, we briefly explore the value of an acid-ethanol extraction stage.

RESULTS AND DISCUSSION

Comparisons of Oxidized Lignin Solubility with E-Stage Delignification

Alkali solubility measurements were performed on an oxidized lignin that was isolated from the caustic extraction effluent of an aqueous DE bleach sequence. [Details on the oxidized lignin are given in the Experimental Section.] One might expect this oxidized lignin to be soluble in water. Indeed, the lignin was so soluble in aqueous ~0.07 M NaOH that it had not reached the saturation limit when the concentration was increased to 22 g/L. Additional experiments to determine the alkali solubility of this lignin in water were not performed due to the limited amount of the isolated lignin available. The solubility of the oxidized lig-

nin decreased by an order of magnitude, from 2.8 to 0.25 g/L, as the ethanol content in the ~0.07 M NaOH medium was increased from 50 to 75% (Fig. 1, curve A). It was very sparingly soluble in absolute ethanol (~0.060 g/L). Clearly, the presence of high concentrations of ethanol (>50%) adversely affected the solubility of the D_0 lignin under alkaline conditions.

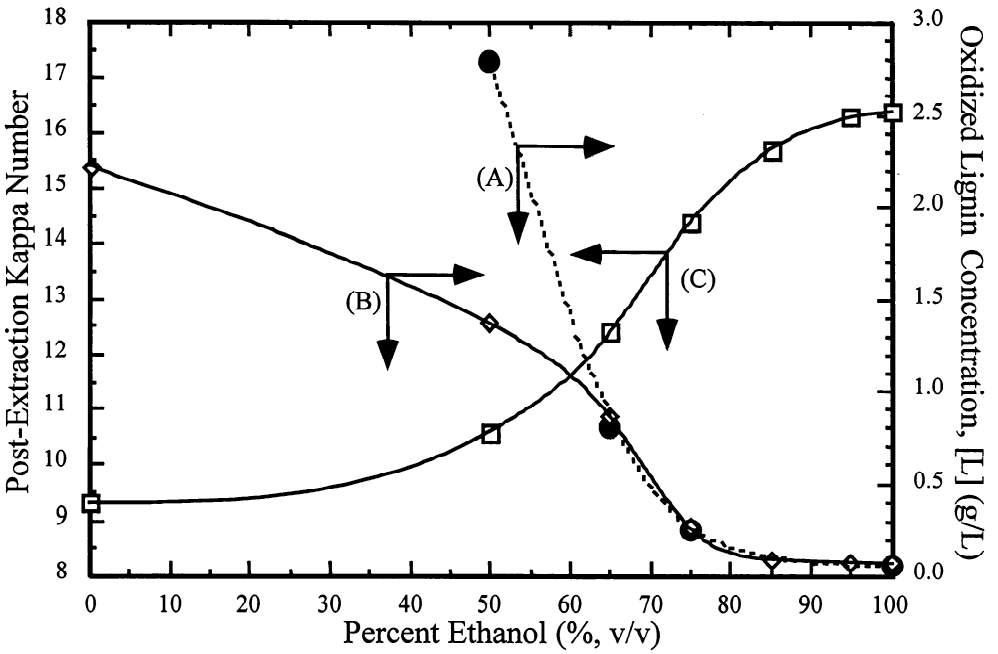


Figure 1. Comparisons of the effect of ethanol concentration on oxidized lignin solubility (●, curve A), dissolved lignin concentration in E-stage effluents (◇, curve B), and post-extraction kappa number (□, curve C).

Comparisons were also made between the measured lignin solubility and lignin concentration in the E-stage effluents, and the measured post-extraction kappa numbers of the pulp in the various media to determine if solubility limits delignification. Curve B in Figure 1 displays the concentration of oxidized lignin, [L], observed in the medium consistency E-stage effluents performed with various ethanol-water solutions. The corresponding kappa number of the extracted pulp is also given in Figure 1 (curve C). The amount of oxidized lignin in the effluents

decreased sharply, from 1.4 g/L to 0.25 g/L, as the ethanol concentration in the extraction medium was increased from 50 to 75%. The [L] in the E-stage effluents (curve B) and the kappa numbers (curve C), as shown in these figures, are complementary; i.e., the [L] decreases as the kappa number increases.

Interestingly, at high ethanol concentrations (i.e., >50%), the oxidized lignin solubility (curve A) coincided with the [L] levels in the E-stage of the corresponding medium. The post-extraction kappa number sharply increased just as lignin solubility decreased abruptly. These results suggested that the solubility of oxidized lignin limits lignin removal during E-stages conducted in ethanol-rich (>50%) media. Comparisons also showed that the alkali solubility of D_0 lignin was much higher in water than in 50% ethanol (>22 g/L vs. 2.8 g/L, respectively). The [L] level in the 50% E-stage effluent was approaching the saturation capacity of the medium and was starting to restrict E-stage lignin removal.

Effects of a Second Caustic Extraction with Water

Several additional tests were performed with the pulp extracted with the 100% ethanol E-stage to further examine the solubility issue. Washing the ethanol E-stage pulp with deionized water instead of ethanol resulted in ~4 unit kappa number drop, from 16.3 to 12.1. Performing a second aqueous E-stage on this washed pulp caused the kappa number to decrease to 9.5. This re-extracted kappa number is close to the post-extraction kappa number obtained with a single 100% aqueous E-stage.[5,6] Clearly, the data strongly supports the conclusion that E-stage delignification is limited by oxidized lignin solubility in ethanol-rich media.

Explanations for Observed Alkali Solubility Behavior of Oxidized Lignin

The observed solubility behavior of oxidized lignin in ethanol-water solutions, however, differs from what we initially expected based on various reports on

solvent-based pulping processes.[1,2,5,8] Ni and van Heiningen[2] demonstrated that additional lignin can be leached from Alcell® brownstocks if the pulps are washed with solutions containing >60% (v/v) ethanol instead of water. In addition, Ni and Hu[5] have shown that the maximum solubility of Alcell® lignins in ethanol-water solutions occurs with 70 to 85% (v/v) ethanol, which corresponds closely with the previous leaching study results. VanBeckum and Ritter[9] reported in the late 1930s that hot ethanol, in combination with 3% monoethanolamine, was very efficient at solubilizing and removing oxidized lignin from chlorinated sawdust residue. Later investigators adapted this holocellulose pulping method to selectively delignify unbleached pulps for cellulose chemical analyses, such as alpha-cellulose and viscosity determinations.[10]

The apparent discrepancy between the solubility behavior of Alcell® lignins and D_0-stage lignins could be explained by the strong coulombic molecular interactions that prevail in the E-stage between the solute (i.e., lignin) and solvent.[11,12] Under the alkaline conditions of the E-stage, the carboxylic acid groups contained in the oxidized lignin are ionized. Carboxylate anions are generally less soluble in ethanol than their protonated forms, and are typically more soluble in water than in ethanol (Table 1).[13] Water, with its high dielectric constant (ε=78), is much more effective than ethanol (ε=25) at stabilizing and solvating the charged carboxylate anions; improved charge stabilization would, in turn, assist the dispersion and dissolution of the oxidized lignin into solution.[11,12] Lignosulfonates, which contain ionized sulfonic acid groups, exhibit similar solubility behavior to that of ionized D_0 lignins (i.e., lower solubility in ethanol or ethanol-water solutions as compared to water).[14]

Ethanol leaching of Alcell® pulps, unlike the caustic extraction stage, is conducted at slightly acidic to neutral conditions[1,2] where the ionizable acids in lignin, such as phenolic and carboxylic acid groups, exist in their protonated forms. Under these conditions, other solute-solvent molecular interactions, such as van der

Table 1. Solubility of various carboxylic acids and corresponding sodium salts in water and ethanol.[13]

	Solubility (g solute/L solvent)			
	Water		Ethanol	
	-COOH	-COONa	-COOH	-COONa
Formic/Formate	miscible	769	miscible	slightly soluble
Benzoic/Benzoate	16.6	556	435	13
Salicylic/Salicylate	2.2	1110	370	109
Oxalic/Oxalate	143.0	37	400	insoluble
Succinic/Succinate	77.9	200	54	insoluble

Waals, dispersion, and hydrogen bonding, have a much greater influence on the solubility of lignin in a given medium. These weaker molecular interactions are overshadowed by ionic interactions when the solute is ionized in the solvent.[11,12]

Acid Ethanol Extraction

Closer examination of the data in Table 1 reveals that non-ionized carboxylic acids are typically more soluble in ethanol than in water. We suspected, based on the above reasoning, that oxidized lignin may likewise be more soluble and extractable in an acidic, ethanol-rich medium than water. To test this hypothesis, we extracted a D_0-treated pulp with an acidic extraction stage (A_E-stage) with various ethanol-water mixtures (Fig. 2).[7] Increasing the ethanol concentration facilitated lignin removal from the D_0-treated pulp. The greatest delignification occurred when the extraction media contained 90% ethanol.

Correlations of Acid Extraction Performance to the Solubility Parameter Analysis

The results of the acid extraction experiments suggested that the solubility of non-ionized D_0 lignin was improved as the ethanol concentration was increased in

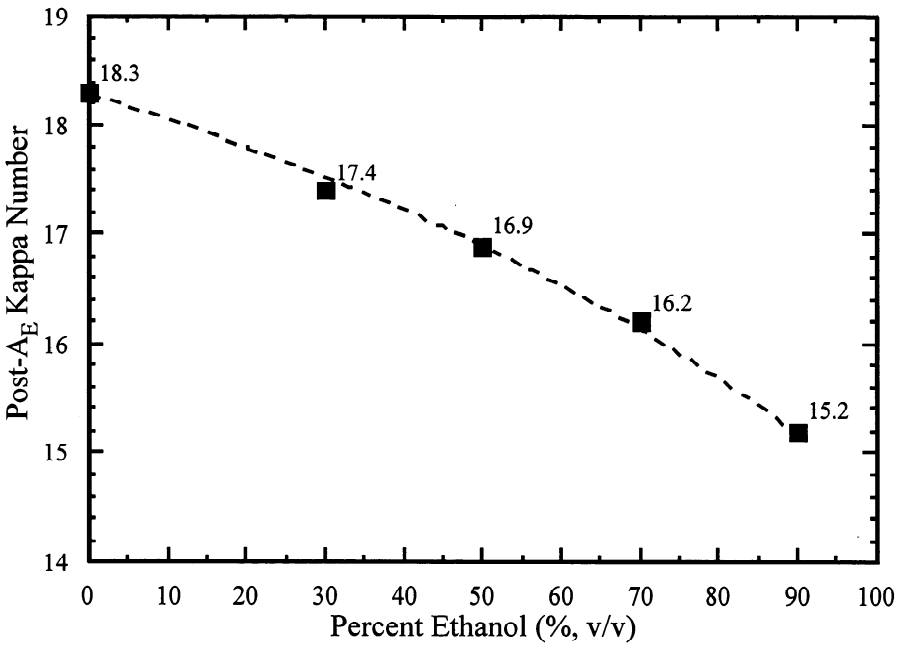


Figure 2. The influence of ethanol concentration in an acidic extraction stage on a D_0-treated pulp with an initial kappa number of 19.3, under the following conditions: 0.01 M $[H^+]$; 1.25% consistency; 70°C; and t =5 hrs.[7]

the extraction medium. To better understand this finding, we estimated the solubility parameter of the D_0-stage lignin and compared it to the solubility parameters of the various ethanol-water mixtures to see if there were any correlations to acid extraction performance.

Several studies have demonstrated that good solvents for non-ionized lignin typically have solubility parameters that are close to those of lignin, and have strong hydrogen bonding capacity.[5,8] The solubility parameter is defined as:

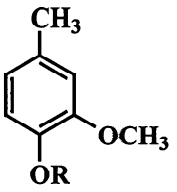
$$\delta = \left(\frac{\Delta E_v}{V}\right)^{1/2} = \left(\frac{\sum \Delta e_i}{\sum v_i}\right)^{1/2} \qquad (1)$$

where ΔE_v is the energy of vaporization at zero pressure and V is the molar volume of the solvent or polymer. The square of the solubility parameter is often referred to as the cohesive energy density and is a relative measure of the solvent-solvent or

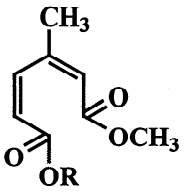
the solute-solute attraction strength.[11] Several empirical methods exist for estimating the solubility parameter for organic compounds and polymers.[5,8,11,15] One approach, developed by Fedors,[15] examines the atomic and functional groups that comprise the compound or polymer. The solubility parameter is calculated by summing the individual contributions that atomic and functional groups (Table 2) have on ΔE_v and V (Eq. 1, far right-hand expression).

Table 2. Atomic and functional group contributions to the molar vaporization energy (Δe_i) and molar volume (v_i), according to Fedors.[11,15]

Atomic/Functional Group of Compound(i)	Δe_i (J/mol)	v_i (cm ^{3}/mol)
-CH_3	4,710	33.5
-CH_2-	4,940	16.1
>CH-	3,430	-1.0
-HC=	4,310	13.5
>C=	4,310	-5.5
-COOH (carboxylic acid group)	2,760	28.5
-COO- (ester group)	1,800	18.0
>C=O	17,400	10.8
-O-	3,350	3.8
-OH	29,800	10.0
Ring Conjugated Bonds (for each = bond)	1,670	-2.2
Ring Closure (for 5 or more atoms)	1,050	16.0
Phenyl group (tri-substituted)	31,900	33.4



1 R=OCH_3
2 R=H



3 R=OCH_3
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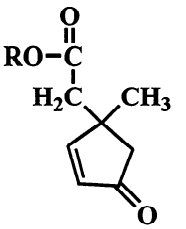
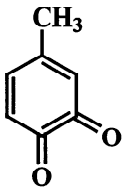


5 R=OCH_3
6 R=H



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Solubility parameters were estimated for several different lignin models (**1**-**7**, Table 3) using the method described by Fedors.[5,11,15] Compounds **1** and **2** were selected to represent the etherified and free phenolic structures contained in softwood kraft lignins; these had δ-values of 19.3 and 25.0 $(J/cm^3)^{1/2}$, respectively. A δ-value for kraft lignin was estimated from the δ-values of **1** and **2** to be between 21 to 21.6 $(J/cm^3)^{1/2}$. This estimated δ-value was based on the weighted average of etherified and free phenolic structures that have been observed for kraft residual lignins, namely 30 to 40 phenolic groups per 100 phenylpropane units.[16-19] The estimated δ-value was close to the 22.6 $(J/cm^3)^{1/2}$ value reported by Schuerch[8] for kraft lignins.

Table 3. Calculated solubility parameters for various model structures for D_0 oxidized lignins.

Model Structures in D_0 lignins	Solubility Parameter $[(J/cm^3)^{1/2}]$
1	19.3
2	25.0
3	25.0
4	28.6
5	22.4
6	24.9
7	29.6

Chlorine dioxide oxidation of lignin affords muconic acids (**3** and **4**), related lactones (**5** and **6**), and quinonoid structures (**7**), according to various lignin model studies.[20-24] In general, the δ-values of compounds **3**-**7** were either the same or slightly higher than the δ-value for phenolic structure **2**. The solubility parameter of D_0 oxidized lignin was estimated to be between 21 to 23.4 $(J/cm^3)^{1/2}$ based on the conversion of phenolic structures to muconic acids, lactones, and/or quinone structures.

Next, the δ-values for the various ethanol-water solutions were recalculated on a volume basis from the data in the Ni and Hu study[5] (Fig. 3) and compared to

the estimated δ-value of oxidized lignin. The δ-value of oxidized lignin was close to the δ-values of ethanol-water solutions containing ≥90% ethanol; this result suggests that non-ionized lignin is more soluble in ethanol than in water. Indeed, we have found that, at an acid concentration of ~10^{-2} M, the isolated oxidized lignin had a solubility of 2.3 g/L in ethanol, but only 1.7 g/L in water.[7] In addition, the performance of the acid extraction stage (Fig. 2) improved as the δ-value of the ethanol-water solution approached the estimated δ-value of oxidized lignin.

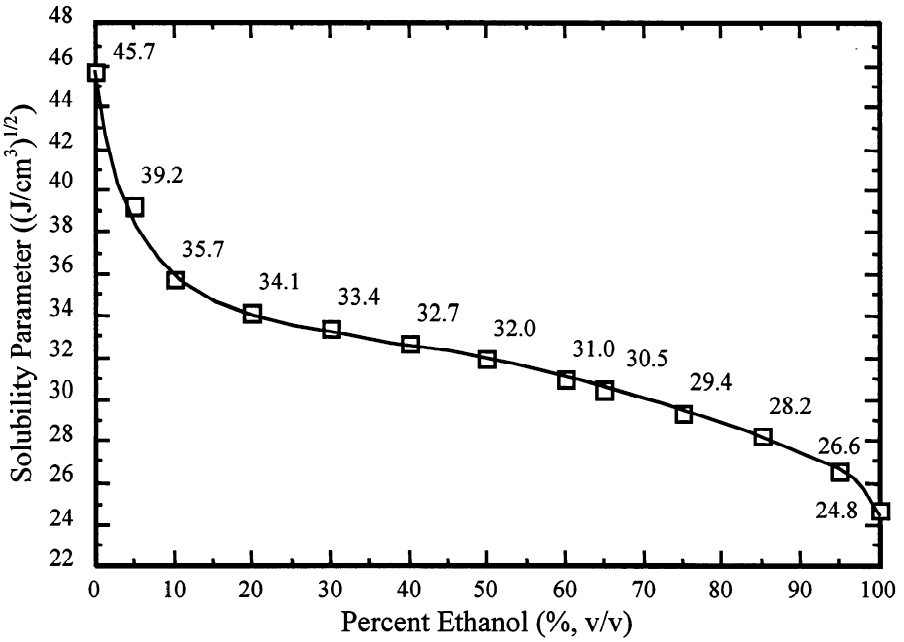

Figure 3. Calculated solubility parameters for various ethanol-water solutions as a function of ethanol concentration.

Acid vs. Alkaline Extraction Stage Delignification

Looking back at the data from the various lignin extraction stages (Figs. 1 and 2), we see that an aqueous caustic extraction stage is more efficient at lignin removal than an acid ethanol extraction stage. This observation may reflect the slower dissolution of oxidized lignin with the weaker solute-solvent molecular in-

teractions present in acid ethanol extraction as opposed to the stronger ionic molecular interactions present in aqueous caustic extraction.[11,12,25] We will, in subsequent reports, optimize the delignification conditions of the acid ethanol extraction stage,[26] and examine the impact of this novel extraction stage on subsequent pulp bleachability.[27]

CONCLUSIONS

The solubility of oxidized lignin under alkaline conditions sharply decreases as the ethanol concentration is increased from 50 to 75%. The rapid reduction in alkali D_0 lignin solubility corresponds well with observed lignin concentration in alkaline extraction effluents with ethanol-water solutions. The decrease in delignification with ethanol-rich solutions (>50%) appears limited by the alkali solubility of oxidized lignin in these media. This behavior is likely related to the medium's ability to interact with *ionized* polar groups, such as carboxylates, that are on the oxidized lignin.

There are some important implications from this study that can apply to solvent-assisted bleaching sequences. A caustic extraction stage following D_0 or other oxidation stage will be ineffective at lignin removal if the extraction medium contains high concentrations of ethanol [>50% (v/v)]. However, the solubility behavior of *non-ionized* carboxylic acids and the results of our solubility parameter analysis predict that oxidized lignin will be more soluble in ethanol under acidic conditions. Our initial tests with acid extractions of D_0-treated pulps indicated that 90% ethanol medium was more effective than a totally aqueous medium at lignin removal. Future studies will examine acid extraction stages with ethanol-water solutions[26] and its impact on pulp bleachability.[27] The use of an ethanol-rich medium in an E-stage, although ineffective at lignin removal, may provide a valuable tool for investigating caustic extraction chemistry.

EXPERIMENTAL

Chlorine Dioxide and Extraction Stages

A conventional kraft pulp (southern pine) was obtained from a mill and used throughout this study. Additional details about the pulping conditions are provided in previous reports.[6,7] The D_0-stage was performed on a 29.3 kappa pulp at the following conditions: 1.79% ClO_2 on o.d. pulp (0.16 kappa factor), 3% consistency (100% aqueous), initial pH 4.2-4.6 prior to ClO_2 addition, 45°C, 30 min reaction time, and an end pH of 2.4. This treatment yielded a pulp of kappa number 19.5.

General caustic extraction conditions were as follows: 2.58% NaOH on pulp (0.55 caustic multiple), 10% consistency, 60°C, and 60 minutes reaction time. Extractions were performed in Kapak®/Scotchpack heat-sealable pouches with various media. After extraction, the effluents were separated from the pulp fibers (prior to washing); the effluents were placed in an amber reagent bottle and stored at 5°C until needed. The pulps were washed with 130 mL/o.d. g of pulp of the corresponding medium (without alkali). Residual lignin content in the pulps was determined by micro-kappa number measurements (TAPPI Useful Method UM-246).

Selected pulps from E-stages utilizing absolute ethanol were subjected to a second E-stage to examine the influence alkali D_0 lignin solubility. These pulps, prior to re-extraction, were washed with copious amounts of deionized water. Afterwards, the pulps were re-extracted under conditions similar to those of the previous E-stage using a totally aqueous medium.[7]

Acid ethanol extraction (an A_E-stage) was performed on the above D_0-stage treated pulp. Experiments were conducted at 1.25% consistency using various ethanol-water solutions at 70°C. Reactions were conducted in a sealed container that was heated using a water bath. The pulps were extracted for 5 hours, and afterwards were drained of extraction effluent to ~25% consistency.[7]

Isolation of Oxidized Lignin from Caustic Extraction

Approximately 150 o.d. g of a conventional softwood kraft pulp was subjected to an aqueous DE bleaching sequence under conditions similar to those listed above. The resulting pulp had a post-extraction kappa number of 8.5. The extraction effluent (~1.1 L) was separated from the pulp using a Büchner funnel and freeze-dried to yield ~1.9 g of organic material.[7]

A sample of this material was subjected to an acid hydrolysis in accordance with TAPPI Standard T-249 cm-85 and the resulting hydrolyzate was analyzed for carbohydrates using the HPLC analysis method of Kaar *et al.*[28] Results from the above analysis indicated that the isolated oxidized lignin contained ~7% carbohydrate material that was primarily composed of glucose, xylose, and galactose monomeric units.[7] The small amount of carbohydrates in the isolated lignin is comparable to the amounts recently reported by Fuhrmann *et al.*[29] in ClO_2-based bleaching effluents.

Solubility Measurements

Aqueous oxidized lignin solutions ranging from 0.015 to 0.15 g/L were made by using the above isolated, freeze-dried material. Absorbance measurements were made with these solutions, under similar alkaline conditions of the E-stage (~0.07 M NaOH), using a spectrophotometer operating at a 260 nm wavelength. The amount of [L] (in g/L) was correlated with the 260 nm absorbance, A_{260}, using the Beer-Lambert relationship. An absorptivity value for the oxidized lignin was determined to be 14.7 L/(g•cm) from the above calibration curve.[7]

The solubility of the isolated lignin was measured in various ethanol-water media as follows. Approximately 25 mg of the freeze-dried material was weighed into a 5-mL volumetric flask. To this flask was added the alkaline medium of interest (~0.07 M NaOH) to the mark. The contents of the flask were stirred at room

temperature for 60 minutes. [A 60-minute stirring time was chosen based on the 60 minutes used for the E-stage.] Afterwards, the solution was centrifuged to remove any suspended solids. The supernatant was collected and diluted with ultrapure deionized (DI) water at several different concentrations. The A_{260} values of the solutions were measured, and [L] was determined from the dilution factor. This was repeated in triplicate and the results averaged to give the solubility values shown in Figure 1. It was assumed that both the dissolved and undissolved components that comprise the oxidized lignin have the same absorptivity value. Reported solubility values had a coefficient of variation of ≤10%.[7]

The [L] in the various E-stage effluents, produced from the earlier study,[6,7] were determined as follows. Known volumes of the effluents were diluted with ultrapure deionized water to three different concentrations, and the A_{260} values were determined. The average amount of [L] in the effluents was calculated from the A_{260} and the dilution factor. Reported values had a coefficient of variation of ≤10%.[7]

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REFERENCES

1. Hergert, H.L. and Pye, E.K., "Recent History of Organosolv Pulping", *TAPPI Solvent Pulping Symp. Proc.*, Boston, MA, 9 (1992).

2. Ni, Y. and van Heiningen, A.H.P., "Lignin Removal from Alcell® Pulp by Washing with Ethanol and Water", *Tappi J.* 79(3):239 (1996).

3. Ni, Y., van Heiningen, A.R.P., Lora, J.H., Magdzinski, L. and Pye, E.K., "A Novel Ozone Bleaching Technology for the Alcell® Process", *J. Wood Chem. Tech.* 16(4):367 (1996).

4. Solinas, M. and Murphy, T., "Ozone Selectivity Improved with Use of Organic Solvent", *Pulp & Paper* 70(3):133 (1996).

5. Ni, Y. and Hu, Q, "Alcell® Lignin Solubility in Ethanol-Water Mixtures", *J. Appl. Polym. Sci.* 57:1441 (1995).

6. Brogdon, B.N., Dimmel, D.R. and McDonough, T.J., "The Influence of the Bleaching Medium on Caustic Extraction Efficiency (I): The Role of Fiber Swelling", *J. Pulp Paper Sci.* 23(10):J499 (1997).

7. Brogdon, B.N., *Effects of Ethanol Media on Chlorine Dioxide and Extraction Stages for Kraft Pulp Bleaching*, Ph.D. Dissertation, IPST, Atlanta (1997).

8. Schuerch, C., "The Solvent Properties of Liquids and Their Relation to the Solubility, Swelling, Isolation and Fractionation of Lignin", *J. Am. Chem. Soc.* 74:5061 (1952).

9. VanBeckum, W.G., and Ritter, G.J. Rapid Methods for the Determination of Holocellulose and Cross and Bevan Cellulose in Wood. *Paper Trade J.* 105(18):127 (Oct. 28, 1937).

10. UM 249 -- Delignification of Unbleached Pulp (Chlorine Gas Method). *TAPPI Useful Methods 1991*, Atlanta, TAPPI Press, 1990.

11. Barton, A.F.M., *CRC Handbook of Solubility Parameters and Other Cohesion Parameters,* Boca Raton, CRC Press Inc., 1983.

12. Reichardt, C. *Solvent Effects in Organic Chemistry.* New York, Verlag Chemie, 1979. Chapts. 4 and 5.

13. Windholz, M., *The Merck Index,* 10th Ed., Rahway, NJ, Merck & Co., 1983.

14. Luh, S.P. and Frederick, W.J., "Phase Behavior of Sodium Lignosulfonates in Water-Ethanol Mixtures", *Holzforschung* 46(4):325 (1992).

15. Fedors, R.F., "A Method for Estimating Both the Solubility Parameters and Molar Volumes of Liquids", *Polym. Eng. Sci.* 14(2):147 (1974).

16. Gellerstedt, G. and Lindfors, E.. "On the Structure and Reactivity of Residual Lignin in Kraft Pulp Fibers", *International Pulp Bleaching Conference Proceedings*, Stockholm, Sweden, June 11-14, SPCI, Vol. 1, p. 73 (1991).

17. Froass, P.M., *Structural Changes in Lignin During Kraft Pulping and Chlorine Dioxide Bleaching.* Ph.D. Dissertation, IPST, Atlanta (1996).

18. Gellerstedt, G., "Chemical Structure of Pulp Components", In: *Pulp Bleaching: Principles and Practice*, C.W. Dence and D.W. Reeve, Eds., Atlanta, TAPPI Press, 1996.

19. Froass, P.M., Ragauskas, A.J. and Jiang, J., "Chemical Structure of Residual Lignin from Kraft Pulp", *J. Wood Chem. Technol.* 16(4):347 (1996).

20. Dence, C.W., "Chemistry of Chemical Pulp Bleaching", In: *Pulp Bleaching: Principles and Practice*, C.W. Dence and D.W. Reeve, Eds. Atlanta, TAPPI Press, 1996.

21. Gierer, J., "Basic Principles of Bleaching -- Parts I and II", *Holzforschung* 44(5):387 and 44(6):395 (1990).

22. Brage, C., Eriksson, T. and Gierer, G., "Reactions of Chlorine Dioxide with Lignins in Unbleached Pulps. Part I", *Holzforschung* 45(1):23 (1991).

23. McKague, A.B., Reeve, D.W. and Xi, F., "Reaction of Lignin Model Compounds Sequentially with Chlorine Dioxide and Sodium Hydroxide", *Nord. Pulp Pap. Res. J.* 2:114 (1995).

24. Ni, Y., Shen, X. and van Heiningen, A.R.P., "Studies on the Reactions of Phenolic and Non-Phenolic Lignin Model Compounds with Chlorine Dioxide", *J. Wood Chem. Technol.* 14(2):243 (1994)

25. Brogdon, B.N., Dimmel, D.R. and McDonough, T.J., "Physico-Chemical Processes Limiting Lignin Removal During Bleaching Extraction", In: *Further Advances in the Forest Products Industries*, AIChE Symp. Series, no. 315, vol. 93, Vol. Editor: P.W. Hart, AIChE, New York, p. 52 (1996).

26. Brogdon, B.N., Dimmel, D.R. and McDonough, T.J., "A Fundamental Study of a Novel Extraction Stage for an Organosolv-Based Bleaching Sequence", In: *Further Advances in the Forest Products Industries*, AIChE Symp. Series, no. 315, vol. 93, Vol. Editor: P.W. Hart, AIChE, New York, p. 42 (1996).

27. Brogdon, B.N., Dimmel, D.R. and McDonough, T.J., "Bleaching of Softwood Kraft Pulps Using an Ethanol-Based Partial Sequence", CPPA/TAPPI Proc. *9th Int'l. Symp. on Wood and Pulping Chem.*, Montréal, Québec, A2-1 (1997).

28. Kaar, W.E., Cool, L.G., Merriman, M.M. and Brink, D.L., "The Complete Analysis of Wood Polysaccarides Using HPLC", *J. Wood Chem. Tech.* 11(4):447 (1991).

29. Fuhrmann, A., Li, X.-L. and Rautonen, R., "Effects of ECF and TCF Bleaching Sequences on the Properties of Softwood Kraft Pulp", *J. Pulp Paper Sci.* 23(10): J487 (1997).